

**POLAROGRAPHIC STUDY OF CADMIUM
5-(Hydroxy-2-(Hydroxymethyl)-4H-Pyran-4-one COMPLEX**

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ABSTRACT

A polarographic study ^{was performed} has been carried out on the products formed in the interaction of cadmium(II) with 5-Hydroxy-2-(Hydroxymethyl)-4H-Pyran-4-one, using varying conditions of pH, supporting electrolyte, and concentration. Measurements using the differential pulse method show that cadmium(II) exhibits a molar combining ratio of complexing agents to cation ranging from 1 to 1 to 3 to 1 depending on the pH and the supporting electrolyte employed.

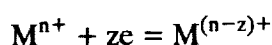
POLAROGRAPHIC STUDY OF CADMIUM 5-(Hydroxy-2-(Hydroxymethyl)-4H-Pyran-4-one COMPLEX

Introduction

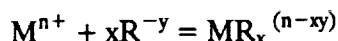
Polarography has been applied variously to the quantitative determination of cadmium in different supporting electrolytes (1). The presence of relatively high concentrations and toxicity of cadmium in process wastewaters which contain phenolic type compounds resulting from coal gasification and liquefaction (1,2) gives rise to a need to study further the coordination chemistry of this metal. Further, the study of the polarography of cadmium could add to the understanding and ascertainment of this element as a possible trace metal in selected lunar like materials. A polarographic study of the interaction of selected organic complexing agents should add to the understanding of cadmium solution chemistry.

This study was undertaken to investigate the formation constants and determine the stoichiometry in a solution of the interaction of cadmium(II) with 5-Hydroxy-2-(Hydroxymethyl)-4H-Pyran-4-one, commonly called kojic acid. The polarographic data obtained using the differential pulse method revealed that the cadmium(II) exhibits complexes ranging from 1 to 1 to 3 to 1 molar ratio of complexing agent to cadmium. The formation constants for the cadmium complexes are supporting electrolyte and pH dependent.

At sufficiently negative potentials, simple and complex ions of cadmium are reduced at the dropping mercury electrode and dissolve in the mercury to produce an amalgam on the surface of the mercury drop. For a reversible electrode reaction involving complex metal ions, Kolthoff and Lingane (3) have shown that the half-wave potentials of metal ions are generally shifted to more negative values by complex ion formation. Further, these authors (3) have derived the relationship for calculating both the formation constant and the coordination number for metal complexes based on this negative shift as a function of the concentration of the complexing agent employed. Thus, according to Kolthoff and Lingane (3) reactions



and



give

$$E_{1/2}^c - E_{1/2}^m = \frac{-0.0591}{z} \log K_f - \frac{-0.0591x}{z} \log C_R \quad (1)$$

where M^{n+} , $M^{(n-z)+}$, R^{-y} , $MR_x^{(n-xy)}$, $E_{1/2}^c$, $E_{1/2}^m$, and K_f , respectively represent the metal ion in oxidation state one, metal ion in state two, complexing agent, metal complex (where x is the coordination number of the metal ion), halfwave potential for the complex, half-wave potential for the simple metal ion, and the formation constant for the complex.

Theory of Phenolic Differential Polarography

Phenolic type compounds are generally strong complexing reagents because in the ionized form they have three pairs of electrons and a negative charge. Further, the stability of metal phenol complex ions is changed markedly by adjusting the pH of the solution. According to the law of mass equilibrium the ionization of phenol type compounds in aqueous media may be represented as follows:



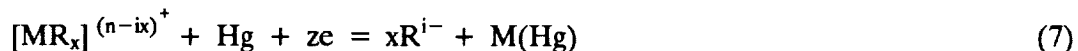
and correspondingly, phenolic metal complex ion formation can be written in the following manner:



The formation constant expression for the above reaction is

$$K_f = \frac{([MR_x]^{(n-ix)+})(H^+)^{ix}}{(M^{n+})(RH_i)^x} \quad (4)$$

For a reversible reduction, at the dropping mercury electrode, to the metallic amalgam state of a complex ion of a metal that is soluble in mercury, one may represent the reaction as follows:



where equation 7 is the sum of equations 5 and 6.

Assuming the activities of mercury and the amalgam to be constant or unified and that molar concentrations may be employed in place of activities in dilute solutions within a moderate concentration range, one may reasonably propose that for phenolic complex ion solutions at constant temperature

$$E_{1/2} = f(\ln C_R, pH) \quad (8)$$

where C_R and C_H are the molar concentrations of the complexing agent and hydrogen ion respectively. Thus within the range of experimental data

$$dE_{1/2} = \left(\frac{\partial E_{1/2}}{\partial \ln C_R} \right)_{pH} dC_R + \left(\frac{\partial E_{1/2}}{\partial pH} \right)_{\ln C_R} dpH \quad (9)$$

Kolthoff and Lingane (3) have shown previously that the effect of complexing agents on the half-wave potential at the dropping mercury electrode is generally to make the half-wave potential more negative. Similarly, based on equations 5 and 6, respectively, the reduction of the simple metal ions and the corresponding complex phenol metal ion at the dropping mercury electrode, one may express the simultaneous effect of complexing agent and pH on the half-wave potential as follows:

$$E_{V_2^c} = E_c^o - \frac{0.0591}{z} \log \frac{([MR_x]^{(n-ix)})^+}{(R^{i-})^x} \quad (10)$$

$$E_{V_2^s} = E_s^o - \frac{0.0591}{z} \log (M^{n+}) \quad (11)$$

$$E_{V_2^c} - E_{V_2^s} = E_c^o - E_s^o - \frac{0.0591}{z} \log \frac{([MR_x]^{(n-ix)})^+}{(R^{i-})^x (M^{n+})} \quad (12)$$

where the subscripts c and s refer to the complex and simple metal ions, respectively, and the superscript o refers to the standard potential of each reaction. The substitution of the molar concentration ratio of the complexing agent ion from equation 4 or 4a into equation 11 gives

$$E_{V_2^c} - E_{V_2^s} = E_c^o - E_s^o - \frac{0.0591}{z} \log K_f \frac{(RH_i)^x}{(H^+)^{ix} (R^{i-})^x} \quad (13)$$

upon combining the $E_c^o - E_s^o$ and the $-0.0591 \log K_f$ terms in equation 13, one obtains equation 1:

$$E_{V_2^c} - E_{V_2^s} = \frac{-0.0591}{z} \log K_f - \frac{0.0591}{z} \log \frac{(RH_i)^x}{(R^{i-}) (H^+)^{ix}} \quad (14)$$

where

$$E_{V_2^c} - E_{V_2^s} = \frac{-0.0591}{z} \log K_f - \frac{0.0591}{z} x \log \frac{(RH_i)}{(R^{i-})} - \frac{0.0591 ix}{z} \log \frac{1}{(H^+)} \quad (15)$$

$$E_{V_2^c} - E_{V_2^s} = \frac{-0.0591}{z} \log K_f - \frac{0.0591}{z} x \log \frac{(RH_i)}{(R^{i-})} - \frac{0.0591 ix}{z} \text{pH} \quad (16)$$

Based on the above equation both pH and concentration of the complexing agent will cause the half-wave potential, $E_{V_2^c}$, of phenolic complexes to shift to more negative potentials. Moreover, it should be noted that neither the concentration of the metal complex nor the simple metal ion is a factor in equation 15; thus $E_{V_2^c}$ is not a function of these ions. However, equation 4 shows that the ratio of the concentration of complex to simple ion

$$\frac{[MR_x]^{(n-ix)}^+}{(M^{n+})} = K_f \frac{(RH_i)^x}{(H^+)^{ix}} \quad (4a)$$

is proportional to the ratio of complexing agent to hydrogen ion. Thus $E_{V_2^c}$ is an implicit function of the above ratio and not the concentration of the complex or simple metal ions. If the stability of the phenolic complex ion is a function of pH, then, based on equation 15, as the pH of a series of solutions containing a fixed amount of complexing agent approaches an upper limiting value, the E_{V_2} of the solution should approach a limit of maximum half-wave potential $E_{V_2\text{cm}}$. Similarly, as the pH of the series approaches a lower limit, the E_{V_2} of the solutions should approach a limit of minimum half-wave potential, $E_{V_2(\text{sm})}$, the E_{V_2} of the simple metal ion. At any constant pH, the magnitude of the quantity $E_{V_2(\text{cm})} - E_{V_2(\text{sm})}$ essentially corresponds implicitly to the relative amounts of the complex and simple

metal ions in the solution. The molar concentrations of complex ions and simple ions should be equal at $\partial E_{1/2}/\partial \text{pH}^2 = 0$.

Firstly, the above discussion and theory show that the complexing agent and the pH simultaneously cause the half-wave potentials of phenolic complex ions to shift to more negative potentials, and, secondly, that differential polarographic study of the complex ion chemistry of these ions requires carefully controlled conditions of pH in excess, complexing agent concentration. A third consequence of the aforementioned theory is that a plot of $E_{1/2c} - E_{1/2s}$ or $E_{1/2c}$ vs. pH should give a graph with asymptotic lower and upper limits, a plot of $d(\Delta E_{1/2})/d\text{pH}$ vs. pH should give a parabolic plot, and a plot of $d^2(\Delta E_{1/2})/d\text{pH}^2$ vs. pH should give a graph with both a positive and a negative area.

In order to test the aforementioned theory, a cadmium complex in our laboratory was selected for study.

Experimental

Apparatus and Reagents. All polarographic measurements were obtained at 25°C employing a Sargent-Welch Voltammetric Analyzer Model 7000 Microprocessor. All data were collected using the differential pulse method (2) over the range -0.300 to -0.900 volt using a scan rate of 0.002 volt per second, a drop time of one second, and an excitation energy of 0.02 volt. All solutions were purged with N_2 for 10 minutes.

Standard solutions of cadmium(II) chloride in water were prepared from EM Science atomic absorption standards traceable to National Bureau of Standards. All other reagents employed in this study were reagent grade chemicals.

The effect of complex formation on the polarographic wave of the cadmium(II) complex was determined as follows: To a series of 50 ml volumetric flasks were added the desired volumes of standard cadmium(II) solution, the volume supporting the electrolyte required to give optimum buffer concentration, and varying concentrations of the chelating agent, and the solutions were diluted to volume with water. $\text{Na}_2\text{B}_4\text{O}_7$ supporting electrolyte was employed, and dilute aqueous NaOH or HNO_3 was added drop wise prior to dilution to obtain the final desired pH. These solutions show reproducible differential pulse peaks (used in place of half-wave potentials) within the region of -0.300 to -0.900 volts.

The kojic acid was purified as follows: The chelating agent was recrystallized after being dissolved in boiling ethanol mixed with finely divided charcoal. This solution was filtered while hot and allowed to recrystallize in a refrigerator at about 5°C. After discarding the alcohol, the chelating agent was dried and stored in a dessicator. The white crystallized solid gave a sharp melting point at 153°C.

Discussion

Differential pulse polarographic measurements obtained in these studies show that cadmium(II) reacts with excess chelating agent to form a 1 to 1, 2 to 1 and 3 to 1 cadmium to reagent products. The ionic strength and the activity coefficients of the reducible complex and the complexing agent were

assumed to be constant over the concentration range studied. Thus on rearranging, equation 16 becomes

$$\log K_f = -x \log C_R / C_R^- - ix \text{pH} \frac{z}{0.0591} (E_{V_2c} - E_{V_2m}) \quad (17)$$

and on differentiation, equation 18 is obtained since E_{V_2m} for the simple metal ion is a constant.

$$\frac{\Delta E_{V_2c}}{\Delta \text{pH}} + 0.0591 x \frac{\Delta \log C_R / C_R^-}{\Delta \text{pH}} = \frac{-0.0591 ix}{z} \quad (18)$$

at constant C_R / C_R^-

$$\frac{\Delta E_{V_2c}}{\Delta \text{pH}} = \frac{-0.0591 ix}{z} \quad (19)$$

and at constant pH, equation 16 becomes equation 1

$$\log K_f = x \log C_R + \frac{z}{0.0591} (E_{V_2m} - E_{V_2c})$$

which was used to calculate the formation constant for the cadmium(II) complexes. Since E_{V_2m} for the simple metal ion is a constant, knowing that cadmium(II) is reduced to cadmium metal at the dropping mercury electrode (4) corresponding to a two electron reduction, one can calculate x the molar combining ratio of complexing agent to the central metal ions for varying conditions of pH supporting electrolyte, etc.

Graphical and tabular data are shown in Figures 1 through 5 and Tables 1 through 9 for the systematic study of several cadmium(II) kojic acid complex ions. These results indicate that the composition and stabilities of the cadmium complex ions formed in these interactions, in the presence of excess chelating agent, depend on optimum conditions of pH and the nature of the supporting electrolyte. Figure 1 shows that all of the cadmium complex ions studied are reversibly reduced at the dropping mercury electrode. Graphical representations (Figure 2) and the data in Tables 1, 2, and 3 indicate that the stability and molar combining ratio of kojic acid to cadmium in ammonium hydroxide-ammonium chloride supporting electrolyte decreases as the pH increases. At pH = 8.38, the molar combining ratio of kojic acid to cadmium is 2 to 1. At pH \geq 9.88, the molar ratio is 1 to 1.

In an attempt to obtain some understanding of the separate ligand ion effect in the aforementioned interactions, sodium borate was selected as a non-competing supporting electrolyte. The data in Tables 4, 5, 6, and 7 and Figure 3, employing sodium borate as a non-complexing supporting electrolyte, show that the molar-combining ratio of kojic acid to cadmium is 2 to 1 and does not depend on the pH of the solution in the pH range 9.8 to 10.8. The composite of these data, Tables 1 through 7, suggest that the ammonia molecule and/or the hydroxide ion may compete with kojic acid when relatively large concentrations of the three are present in the same solution. Data for the effect of pH at constant complex ion concentrations in borate medium are shown in Table 9 and Figure 5 as predicted.

The complexing effect of ammonium hydroxide on cadmium(II) in sodium borate supporting electrolyte is shown in Table 8 and Figure 4. Based on the magnitude of the formation constants in the two support-electrolytes, in the absence of knowing the exponential order of the mass law equations,

the cadmium ammine complex appears to be less stable than the cadmium kojic acid complex. The proposed cadmium ammonium hydroxide interaction in sodium borate supporting electrolyte is



which indicates that cadmium exhibits a coordination number of 4 and a combining ratio of 3 to 1 of ammonium hydroxide to cadmium. Further, assuming kojic acid to be a bidentate ligand, one would expect kojic acid to cadmium interaction to give a combining ratio of 2 to 1 corresponding to a coordination number of 4. At a $\text{pH} \leq 8.38$, in ammonium hydroxide-ammonium chloride buffer, the combining ratio of kojic acid to cadmium is 2 to 1. In the interval $8.38 \leq \text{pH} \leq 9.88$, non-whole number combining ratios are obtained which suggest a mixture of complex species, resulting from competing complexation between kojic acid and ammine and/or hydroxide. At a $\text{pH} \leq 9.88$, a combining ratio of 1 to 1 of kojic acid is obtained which suggests that the composition of the complex becomes constant.

Acknowledgment

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TABLE 1

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{\frac{1}{2}}$, Volts	Formation Constant
89	0	34	-0.623	
89	0.79	34	-0.610	5.74×10^5
89	1.74	33	-0.630	5.72×10^5
89	3.16	35	-0.645	5.57×10^5
89	5.01	34	-0.657	5.66×10^5
89	10.00	34	-0.674	5.36×10^5
89	25.00	34	-0.698	5.52×10^5
89	54.95	34	-0.717	5.07×10^5

Supporting Electrolyte: 0.08 M $\text{NH}_3/\text{NH}_4\text{Cl}$ Avg. $K_f = 5.52 \times 10^5 \pm 0.24$

Coordination Number: 2 pH: 8.38

TABLE 2

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{\frac{1}{2}}$, Volts	Formation Constant
89	0	34	-0.666	
89	0.79	35	-0.670	1.74×10^3
89	1.74	34	-0.679	1.58×10^3
89	3.16	34	-0.687	1.62×10^3
89	5.01	34	-0.693	1.66×10^3
89	10.00	33	-0.702	1.66×10^3
89	25.00	34	-0.714	1.70×10^3
89	54.95	34	-0.724	1.70×10^3

Supporting Electrolyte: 0.2 M $\text{NH}_3/\text{NH}_4\text{Cl}$ $K_f = 1.67 \times 10^3 \pm 0.05$

Coordination Number: 1 pH: 9.88

TABLE 3

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	34	-0.704	
89	0.79	34	-0.688	3.63×10^2
89	1.74	33	-0.698	3.63×10^2
89	3.16	34	-0.706	3.70×10^2
89	5.01	34	-0.712	3.72×10^2
89	10.00	34	-0.721	3.77×10^2
89	25.00	34	-0.733	3.80×10^2
89	54.95	34	-0.743	3.82×10^2

Supporting Electrolyte: 0.4M $\text{NH}_3 - \text{NH}_4\text{Cl}$ $K_f = 3.72 \times 10^{-2} \pm 0.006$
 Coordination Number: 1 pH: 10.15

TABLE 4

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	34	-0.527	
89	5.01	33	-0.572	1.33×10^6
89	13.80	33	-0.598	1.34×10^6
89	20.40	34	-0.607	1.27×10^6
89	50.10	35	-0.630	1.23×10^6
89	100.00	34	-0.647	1.17×10^6
89	199.50	34	-0.665	1.20×10^6

Supporting Electrolyte: 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ Avg. $K_f = 1.25 \times 10^6 \pm 0.07$
 Coordination Number: 2 pH: 7.00

TABLE 5

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	34	-0.535	
89	5.01	34	-0.614	1.90×10^7
89	13.80	34	-0.640	1.90×10^7
89	20.40	35	-0.650	1.90×10^7
89	50.10	34	-0.673	1.90×10^7
89	100.00	34	-0.691	1.94×10^7
89	199.50	34	-0.708	1.84×10^7

Supporting Electrolyte: 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ Avg. $K_f = 1.90 \times 10^7 \pm 0.03$
 Coordination Number: 2 pH: 8.00

TABLE 6

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	34	-0.558	
89	5.01	34	-0.632	1.28×10^7
89	13.80	33	-0.658	1.29×10^7
89	20.40	35	-0.669	1.39×10^7
89	50.10	34	-0.692	1.39×10^7
89	100.00	34	-0.710	1.42×10^7
89	199.50	34	-0.727	1.34×10^7

Supporting Electrolyte: 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ Avg. $K_f = 1.35 \times 10^7 \pm 0.06$
 Coordination Number: 2 pH: 9.00

TABLE 7

Cadmium(II) Micromolar	Kojic Acid Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	33	-0.574	
89	5.01	34	-0.633	3.98×10^6
89	13.80	34	-0.658	3.69×10^6
89	20.40	35	-0.669	3.98×10^6
89	50.10	34	-0.692	3.98×10^6
89	100.00	33	-0.710	4.08×10^6
89	199.50	34	-0.727	3.86×10^6

Supporting Electrolyte: 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ Avg. $K_f = 3.93 \times 10^6 \pm 0.15$
 Coordination Number: 2 pH: 10.00

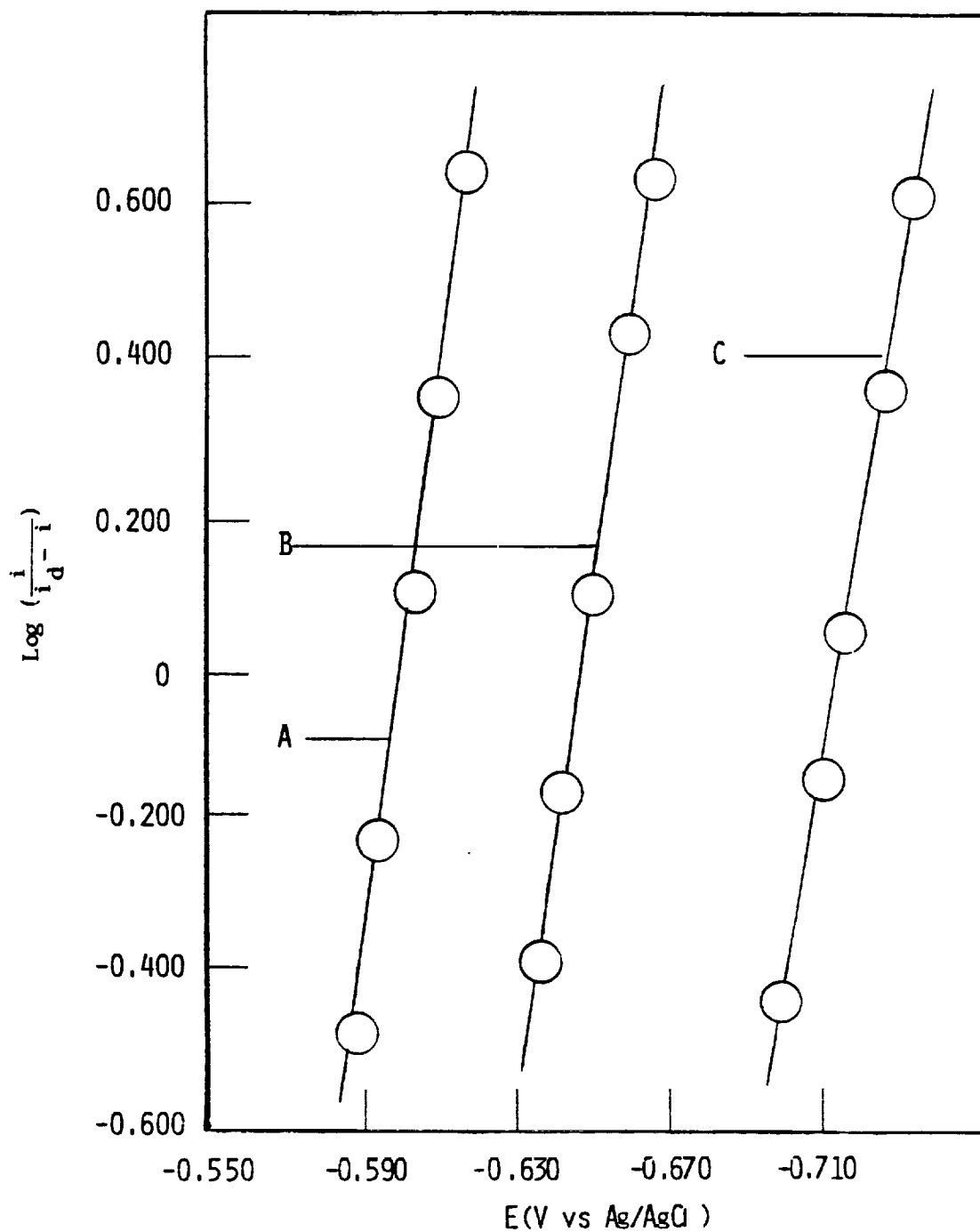
TABLE 8

Cadmium(II) Micromolar	Ammonium Hydroxide Millimolar	Diffusion Current Nanometers	Half-Wave $E_{1/2}$, Volts	Formation Constant
89	0	34	-0.544	
89	30.00	34	-0.572	3.23×10^5
89	50.00	34	-0.591	3.11×10^5
89	100.00	34	-0.618	3.22×10^5
89	150.00	34	-0.634	3.24×10^5
89	200.00	34	-0.645	3.34×10^5
89	251.19	34	-0.654	3.38×10^5

Supporting Electrolyte: 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ $K_f = 3.25 \times 10^5 \pm 0.096$
 Coordination Number: 3 pH: 9.8 to 10.8

TABLE 9

Cadmium(II) Micromolar	Kojic Acid Millimolar	Na ₂ B ₄ O ₇ Millimolar	pH	Diffusion Current Nanometer	Half-Wave E _{1/2} , Volts
89	13.7	30.0	2.00	34	-0.528
89	13.7	30.0	3.00	34	-0.530
89	13.7	30.0	4.00	34	-0.532
89	13.7	30.0	5.00	34	-0.534
89	13.7	30.0	6.00	35	-0.562
89	13.7	30.0	6.50	34	-0.581
89	13.7	30.0	7.00	36	-0.605
89	13.7	30.0	7.50	34	-0.635
89	13.7	30.0	8.00	33	-0.655
89	13.7	30.0	8.50	34	-0.663
89	13.7	30.0	9.00	34	-0.667
89	13.7	30.0	9.50	35	-0.667
89	13.7	30.0	10.00	34	-0.667
89	13.7	30.0	10.50	34	-0.669
89	13.7	30.0	11.00	34	-0.667



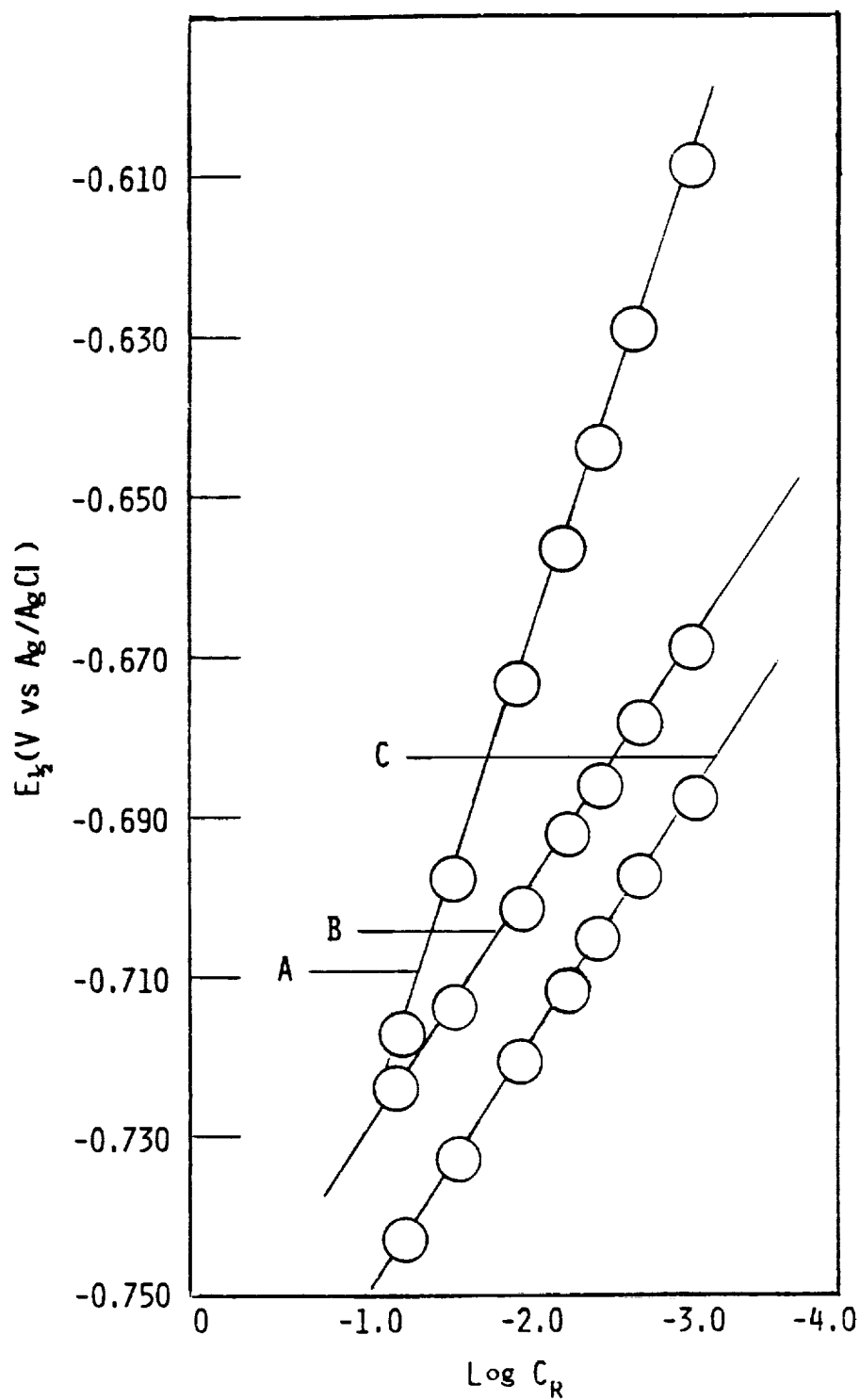
Reversibility Plots:

A — pH — 8.00 — 0.04m $\text{Na}_2\text{B}_2\text{O}_4$ + 89 μm Cd(II) + 13.8m Mol Kojic Acid

B — pH — 10.15 — 0.04m $\text{Na}_2\text{B}_2\text{O}_4$ + 89 μm Cd(II) + 100m Mol NH_4OH

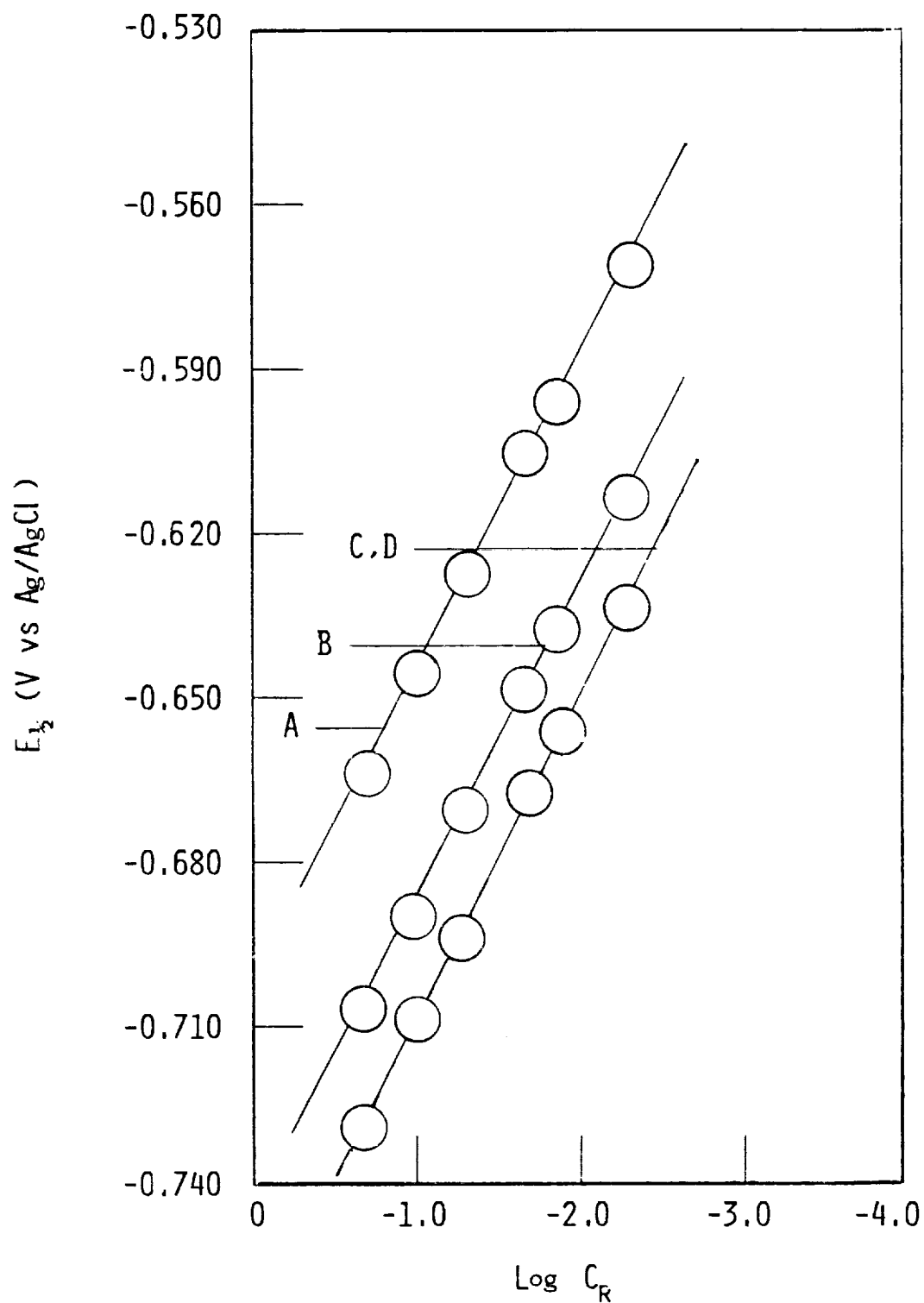
C — pH — 8.38 — 0.08m $\text{NH}_3/\text{NH}_4\text{Cl}$ + 89 μm Cd(II) + 13.8m Mol Kojic Acid

Figure 1



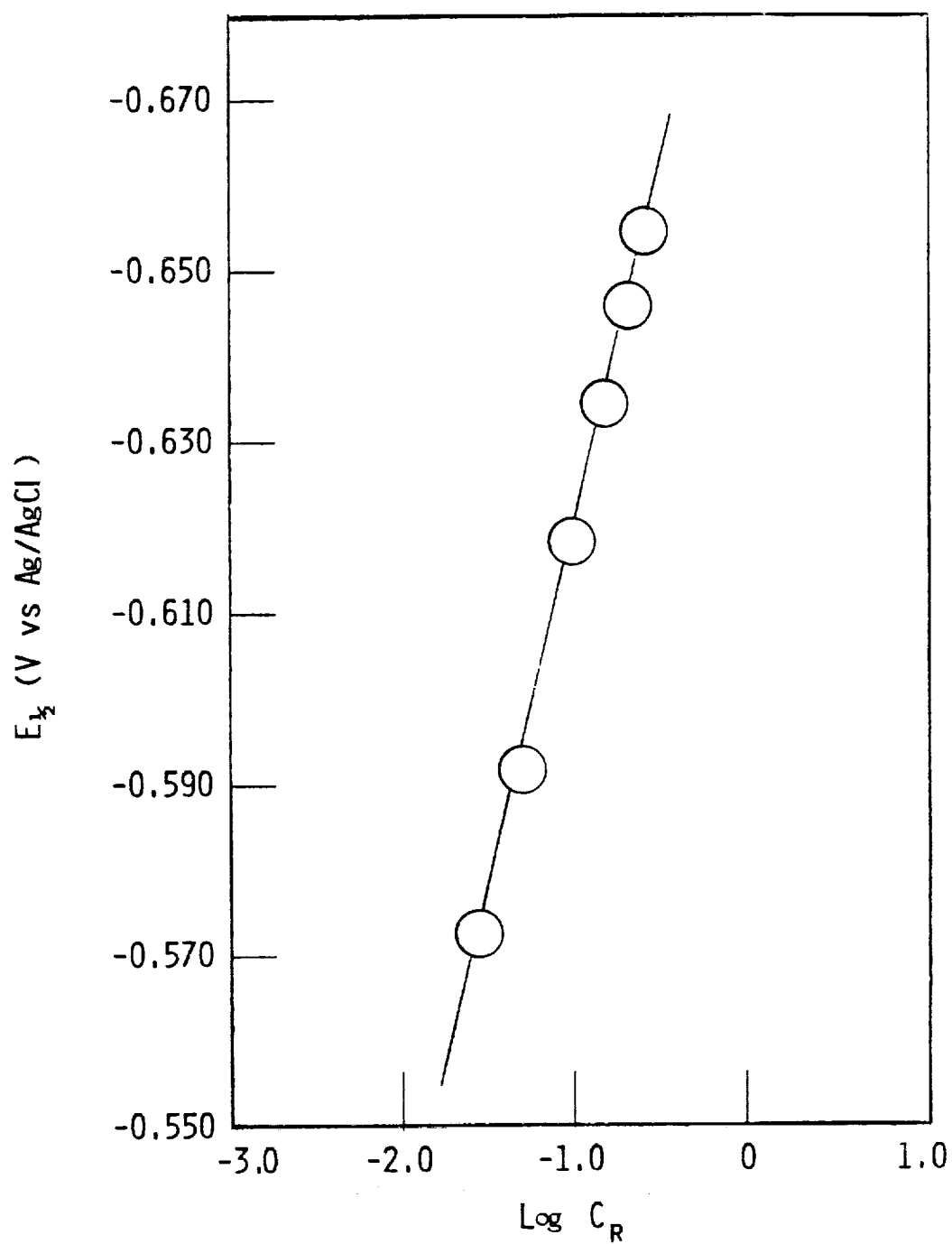
Effects of Complexing Agent Concentration on the Half-Wave Potential of Cadmium in 0.4M $\text{NH}_3\text{-NH}_4\text{Cl}$ at (a) pH-8.38; (b) pH-9.88; (c) pH-10.15

Figure 2



Effects of Complexing Agent Concentration on the Half-Wave Potential of Cadmium in 0.04 M $\text{Na}_2\text{B}_4\text{O}_7$ at (a) pH-7; (b) pH-8; (c) pH-9 and pH-10

Figure 3



Effects of Complexing Agent Concentration on the Half-Wave Potential of Cd(II) in 0.10 M NH_4OH

Figure 4

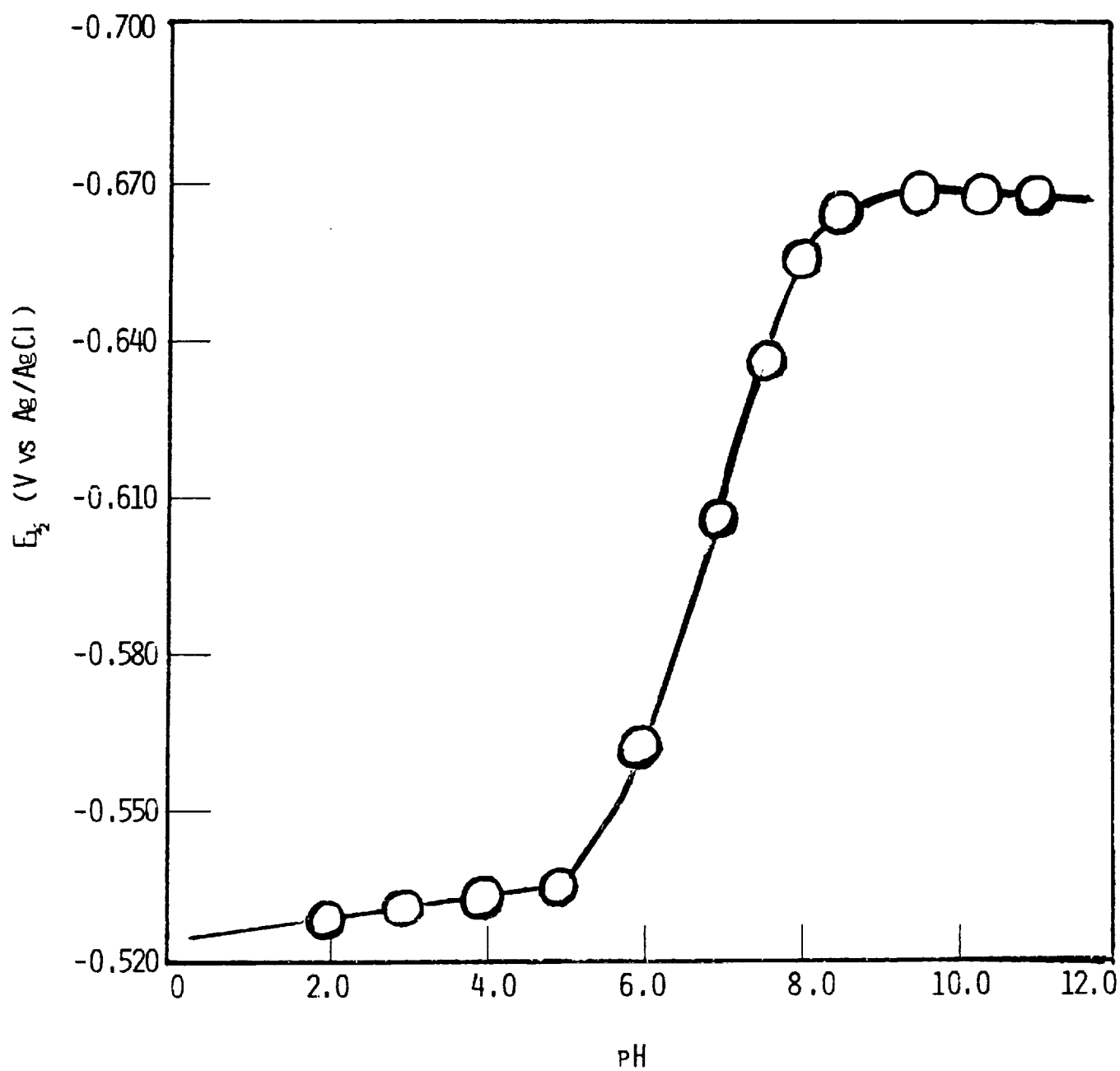


Figure 5